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# A Kinetic Study of CO<sub>2</sub> Adsorption in Cellulose Acetate Membranes

Sarah Hafeez, X. Fan, and Arshad Hussain

**Abstract**—In this research, the CO<sub>2</sub> adsorption study on glassy pure and modified Cellulose Acetate(ca) polymer is conducted to explore, either “dual mode sorption model” of glassy polymers can be supported by pure and modified ca membranes or not. These membranes were fabricated and characterised by SEM and FTIR analysis techniques. According to results, the CO<sub>2</sub> gas was adsorbed by both membranes and adsorption capacity reached the maximum at different pressures. The experimental results were calculated and validated by pseudo first order, pseudo second order and intra-particle diffusion models. According to correlation factor R<sub>2</sub>, the Pseudo second order model was fitted well with experimental data. The experimental and calculated data has confirmed the dual mode sorption model of CO<sub>2</sub> capture in dense pure and modified ca membranes.

**Index Terms**—Cellulose acetate, gas adsorption, pseudo order models, CO<sub>2</sub>, global warming.

## I. MAIN TEXT

In 2005, world CO<sub>2</sub> was estimated as 28051 million metric tons (MMT) and it was estimated that it will reach at 42325 MMT in the year 2030. Other than this, Natural gas reservoirs also need to be purified by capturing CO<sub>2</sub> [1]. The various techniques such as membrane gas separation, cryogenic distillation, amine absorption, and membrane gas absorption and adsorption processes are being implemented to capture CO<sub>2</sub> gas. But membrane gas separation and adsorption processes have been considered and explored more, because of low capital and operation cost, low energy requirement, environment friendly, small foot print and flexibility in handling of higher flow rate, pressure and various feed composition [2].

Since last decade, CO<sub>2</sub> adsorption technique, utilizing particles or fillers as adsorbent, is getting importance day by day. Various adsorbents have been fabricated to study adsorption of CO<sub>2</sub> gas on them. The activated carbon has been extensively utilised due to low cost, thermal stability and less sensitivity towards moisture [3]. On the other hand, single wall, multi wall CNTs [4] and graphene have also been studied thoroughly for CO<sub>2</sub> adsorption. In recent years, Zeolite, alumina [5] and silica [6] have produced remarkable

results in CO<sub>2</sub> adsorption [7], [8]. Lately, Metal-organic frameworks (MOFs) have attracted the attention of many researchers in recent years due to high CO<sub>2</sub> capture efficiency. But the main drawback of low CO<sub>2</sub> selectivity persuades the researchers to work with amine functionalized adsorbents.

With development in this technique, membranes are also considered to be investigated for CO<sub>2</sub> capture by adsorption of gas in membranes. In this regard, different studies have been made such as Zeolite Y membranes were studied by M. T. Sinder *et al.*, for CO<sub>2</sub> adsorption [9]. Zeolite Imidazolate membranes were researched thoroughly for CO<sub>2</sub>/CH<sub>4</sub> adsorption process and I. Inzoli *et al.* has worked on silicalite-1 membrane to know the thermal effects during n-butane adsorption [10]. In 2011 the nano composite (B)-MFI alumina membranes were investigated for CO<sub>2</sub>/N<sub>2</sub> gas adsorption by Nicholas *et al.*, [11]. Interestingly, all the membranes mentioned above, contained pores (meso or nano) which help in adsorption of CO<sub>2</sub>. Surprisingly, no work regarding CO<sub>2</sub> adsorption in dense polymeric membranes has been presented.

The dense polymeric membranes have been used in membrane gas separation applications. The gas transports through these membranes depend upon principle of solution-diffusion mechanism [12], in which the gas molecules absorbed, diffuse and penetrate downstream under pressure gradient. In glassy polymers, dual mode sorption model is used to describe sorption and penetration of gas molecules in glassy polymers. This model consists of a Henry's law 'dissolved' mechanism of gas sorption through polymer and Langmuir 'hole-filling' mechanism, gas adsorption in voids and cavities in glassy polymers [13], [14].

The above mentioned laws are important in a respect that in glassy polymeric membranes, gases sorbed, dissolved and adsorbed. This adsorption can affect the permeability and selectivity of gases through membranes. It can also modify the gas rejection properties of membrane.

In this work, Diffusion Induced Phase Separation (DIPS) technique was utilised to synthesize pure and modified ca membranes by APTMS. The morphological studies were done by SEM, whereas qualitative studies of membranes were done by FTIR analysis. The data was modelled using pseudo first order and pseudo second order models. To complete the kinetics study, intra- particle diffusion model was also studied to explore the steps involved in the gas sorption process.

## II. EXPERIMENTAL

### A. Chemicals

The Cellulose acetate (ca), Acetone, Isopropyl Alcohol,

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APTMS were bought from Sigma Aldrich UK.

## B. Methods

### 1) Modification of CA

The modification of ca was done according to the reported procedure [6]. ca was dissolved in Acetone and then ultrasonicated for 30 minutes after adding APTMS (3-aminopropyltrimethoxysilane). The mixture was magnetically stirred at room temperature for 6 hrs.

### 2) Fabrication of membranes

The membranes were fabricated following the procedure published already [15]. The pure blended membrane was synthesized by dissolving in 1.5 g of ca in 10 ml of acetone kept on stirring. The pure and modified membranes were casted on glass slab after the removal of bubbles in mixture. After casting gelling of membranes was done by dipping membrane is cold water for 20 min. In next step membrane was dipped in hot water 80°C for 30 minutes. Isopropyl alcohol was utilised to dry the membranes. The ca and ca-APTMS modified blended membranes (cap) were considered in this study, which labelled as M (a) and M (b) respectively.

### 3) Setup to study sorption kinetics

The sorption studies of pure and modified membranes were conducted at 25°C under various pressures and time. It was comprised of two gas cylinders such as CO<sub>2</sub> and N<sub>2</sub>, which were connected to the cell through stainless steel pipes. The gases were controlled by Lab Master Pressure regulators. The whole setup was placed in temperature controlled environment with proper exhaust ventilation (Nederman). The flow meters and pressure gauges (Scotia Instrumentation) were connected to record the required flows and pressures during the experiments. The CO<sub>2</sub> (Cozir) sensor was connected at the other end of the setup which ultimately connected with computer to read data. The membrane cell was 2 cm in diameter and designed in a way that it can hold the gas at particular pressure.

At the first stage of the experiment the N<sub>2</sub> gas was passed through membrane cell. The flow was maintained at 100cc/min with 1 bar pressure. In the second stage, membranes were cut in circular shape with diameter of 2 cm. These membranes were regenerated at 120°C. After weighing them, these membranes were mounted in adsorption cell and purged with N<sub>2</sub> for two hours before starting the adsorption studies. The following equation was used for calculating CO<sub>2</sub> adsorption.

$$q = \left( \frac{m_t - m_o}{m_o} \right) \quad (1)$$

where  $q$  is amount of CO<sub>2</sub> adsorbed (mg/g),  $m_o$  is the original mass of adsorbent and  $m_t$  is the mass of adsorbent, at time  $t$ .

## III. RESULTS AND DISCUSSIONS

### A. SEM Analysis

The surfaces of membranes were studied by SEM, S-4700 Hitachi, Japan). SEM images were captured and represented in Fig. 1. The surfaces of membranes were studied at 5000\* magnification, magnifications. The surfaces of pure and

APTMS modified ca membranes are dense and completely smooth.

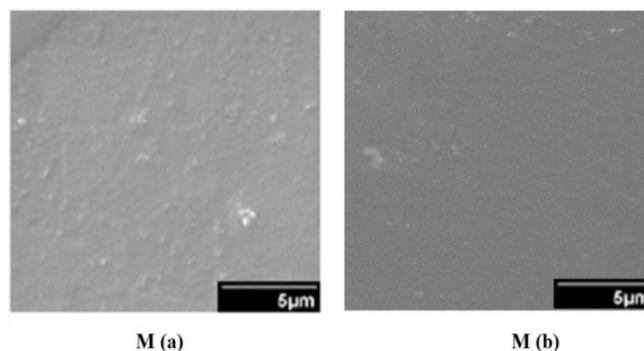


Fig. 1. SEM micrographs.

### B. FTIR Analysis

The qualitative structural analysis of membranes was performed by Fourier Transform Infrared spectroscopy to observe the functional groups in synthesized membranes and represented in Fig. 2. According to the Figure, it can be observed in both spectra, the peaks at 3417cm<sup>-1</sup>, 1790 cm<sup>-1</sup>, 1370 cm<sup>-1</sup> and 1235 cm<sup>-1</sup> are representing the stretching vibration Carboxylic group (-COOH), C=O group, C-CH<sub>3</sub> bond and C-O-C group.

In FTIR spectrum of CA-APTMS M(b), the wide peaks at 3,434 cm<sup>-1</sup>, 1,569 cm<sup>-1</sup> are depicting the presence of NH group confirm the amine functionalization.

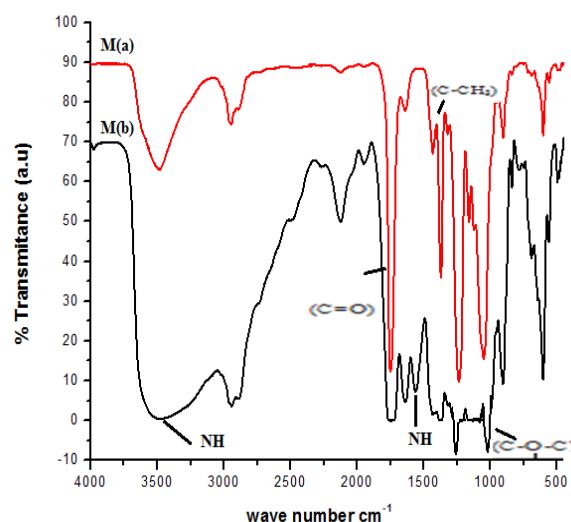


Fig. 2. FTIR spectra.

### C. Adsorption Capacity

Theoretically, adsorption of CO<sub>2</sub> in membranes can be explained by three main steps.

- 1) The gas molecules transport from bulk phase near the surface of membrane.
- 2) The gas gets diffuse into the external surface of membrane.
- 3) Further, gas molecules solubilize in membrane and get adsorb in polymeric chains.

The slower process of the adsorption, determines the overall uptake rate [16]. For this reason, CO<sub>2</sub> gas adsorption and its kinetics were explored. The adsorption isotherms of blended membranes are given in Fig. 3. According to these

Isotherms, both dense membranes have adsorbed CO<sub>2</sub> gas. Interestingly, the CO<sub>2</sub> adsorption in cap (M(b)) blended membrane is high as compared to pure membrane. This modified membrane has the acetate and ester groups of ca and amine functionalization of APTMS, which enhanced the CO<sub>2</sub> affinity. The CO<sub>2</sub> adsorption trend is increasing linearly for both membranes, till it reaches maximum at 1 bar for cap and 1.5 bar for pure ca membrane. However, from 1.5 bar the adsorption of CO<sub>2</sub> become constant.

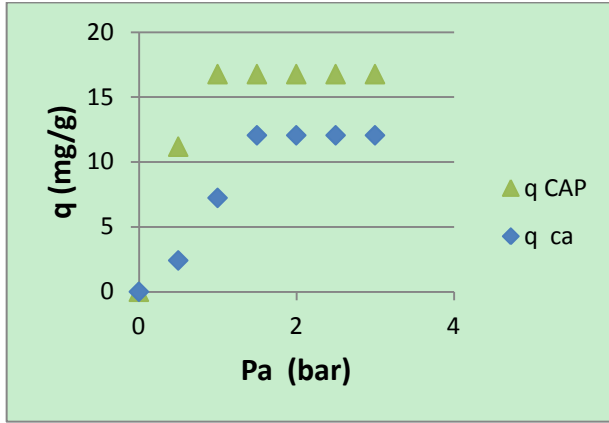


Fig. 3. CO<sub>2</sub> adsorption at pressures.

#### D. Adsorption Kinetics

The time transient CO<sub>2</sub> adsorption profiles of both CA and CA-APTMS are represented in Fig 4. According to this Figure, it can be observed that CO<sub>2</sub> gas has been adsorbed by dense pure CA membrane, which is very attention-grabbing result with respect to dense membranes but modification with APTMS, resulted in NH- functionality in CA membrane. Which resulted in enhanced CO<sub>2</sub> adsorption. This result is very interesting as the NH functionality and free volume has increased uptake of CO<sub>2</sub>.

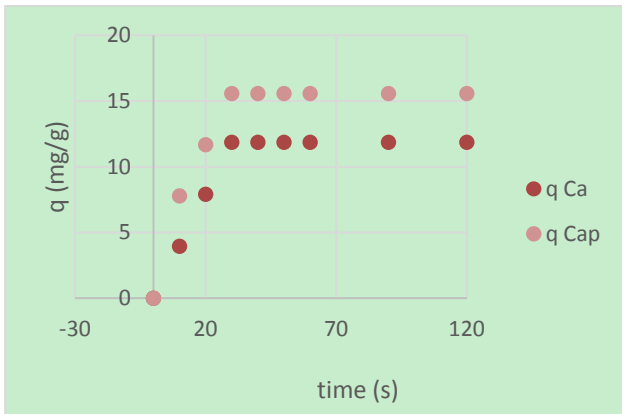


Fig. 4. Time transient CO<sub>2</sub> uptake.

The kinetics were explored by two models represented in the form of two equations, given below. The pseudo first order and second order equations are given as,

$$\log(q_e - q_t) = \log q_e - k_1 t \quad (2)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (3)$$

where  $q_e$  and  $q_t$  (mg/g) are the quantity of CO<sub>2</sub> adsorbed in

membrane at equilibrium and at any time,  $t$  is the time (s) of adsorption. Whereas  $k_1$  (g/mg.s) and  $k_2$  (s<sup>-1</sup>) are the equilibrium rate constant of first and second order pseudo equations. The parameters are calculated by application of pseudo first order and second order on experimental data and tabulated in Table I and II. According to them; the pseudo first order model was not fit very well with the experimental data of both fabricated membranes (see in Fig. 5). The values of  $R^2$  for both membranes are 0.81 and 0.54 respectively.

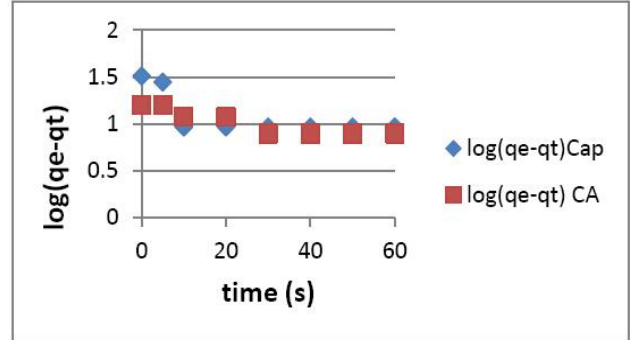


Fig. 5. Pseudo first order model.

TABLE I: PSEUDO-FIRST-ORDER RATE CONSTANTS

Membranes	$K_1$ (s <sup>-1</sup> ) E-3	Rate equation	$R^2$
M(a)	1.0	$\text{Log}(q_e - q_t) = -0.001t + 1.089$	0.54
M(b)	5.0	$\text{Log}(q_e - q_t) = -0.005t + 1.168$	0.81

To confirm either Pseudo second order equation fits well on experimental data of both membranes, the value of  $K_2$  is calculated using pseudo second order model (see in Fig. 6).

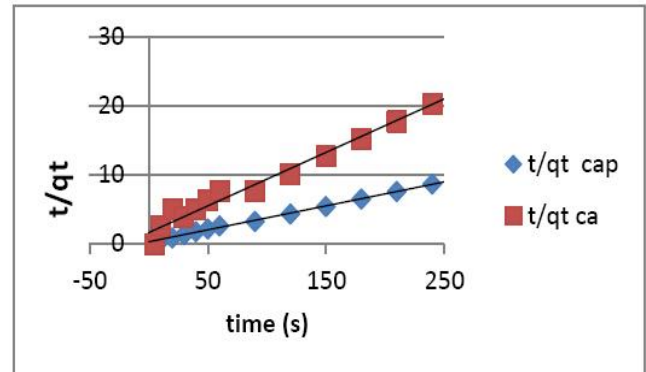


Fig. 6. Pseudo second order model.

The values of correlation coefficient are 0.98 and 0.99. The rate constant  $K_2$  determines the adsorption rate in both membranes. The larger the value of  $K_2$ , slower will be the adsorption rate.

Here  $K_2$  is nearly same, so the adsorption rate in both membranes is also nearly similar.

TABLE II: PSEUDO-SECOND-ORDER RATE CONSTANTS

Membranes	$K_2$ (g/mg.s) E-3	Rate equation	$R^2$
M(a)	3.5	$t/q_t = 0.077t + 1.655$	0.98
M(b)	3.3	$t/q_t = 0.034t + 0.341$	0.99

Other than pseudo first order and second order model,

intra- particle diffusion model is also very essential to explore complete adsorption process. As written above, the adsorption process is based on diffusion of adsorbate from bulk phase to the surface of adsorbent and is followed by diffusion and solubility inside the active places of adsorbent. According to Ho *et al.*, 2000, the intra particle diffusion was given in the form of equation given below.

$$q_t = kt^{\frac{1}{2}} + C \quad (4)$$

where  $q_t$  is the amount of CO<sub>2</sub> amount adsorbed (mg/g) intra in particular time  $t$  (s) and  $k$  is the intra particle rate constant (mg/s). The Fig. 7 represents the plot of  $q_t$  versus square root of time.

In the literature, a straight linear plot is observed for adsorption process which obeys intra particle diffusion mechanism. Which means that particles are obeying only diffusion mechanism during adsorption. On the other hand, according to Fig. 7, the curve is divided into two main steps. This curve is confirming that this adsorption is not exclusively depends upon intra particle diffusion mechanism. The linear increasing region range from 10-40 s is probably due to attraction sorption of gas molecules on the surface of membrane and the region from 40s to onwards be reflecting intra particle diffusion mechanism.

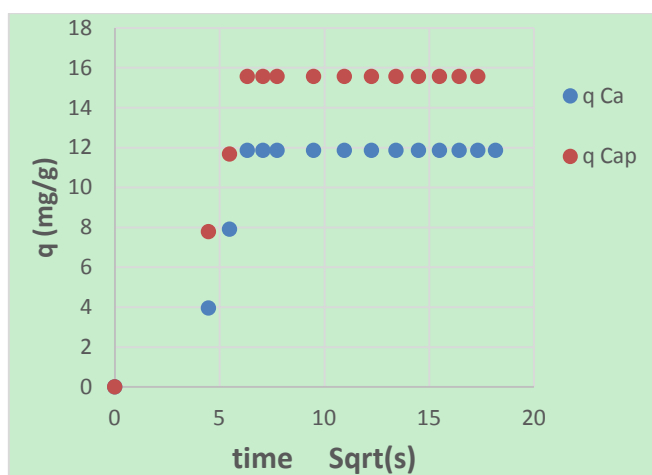


Fig. 7. Intra particle diffusion model.

#### IV. CONCLUSION

Cellulose acetate polymer belongs to the class of glassy polymer. According to literature, glassy polymeric membranes follow the “dual mode sorption model” of gas transport. This model is comprised of two main parts, the dense structure and molecular scale cavities. This shows that there must be chances of CO<sub>2</sub> adsorption in dense membranes. In this research, the pure CA membrane and APTMS modified CA membranes were fabricated to study the gas sorption process through these membranes. The resulting membranes were analyzed by Fourier Transform Infrared Spectroscopy (FTIR) and Scanning Electron Microscopy (SEM). SEM of all membranes reveal smooth and dense surface layer. The CO<sub>2</sub> adsorption study was done on both membranes and surprising results were obtained that CO<sub>2</sub> gas was adsorbed in membranes. But CO<sub>2</sub> adsorption

capacity is high in case of APTMS modified CA membranes which showed that the free volume, OH and NH-functionality have affected the CO<sub>2</sub> adsorption capacity. As CA and APTMS CA membranes are mostly utilised for gas separation processes, so adsorption studies has showed that adsorption capacity of CO<sub>2</sub> can affect the permeability and selectivity of gases. As permeability of gas depends on diffusivity and solubility of gases.

The pseudo first order and second order models were applied to confirm the experimental results of CO<sub>2</sub> adsorption on membranes. The pseudo second order model validated all experimental results as its  $R^2$  value is near 1. The intra particle diffusion model validated that adsorption mechanism in membranes was not one step procedure, it's not the surface phenomena; probably diffusivity and solubility were also involved in CO<sub>2</sub> adsorption. This study is very promising as it reveals that dense polymeric membranes also capture CO<sub>2</sub> by adsorption to purify the environment.

#### ACKNOWLEDGEMENTS

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